

A Novel Cyclic Reaction System Involving CaS and CaSO₄ for Converting Sulfur Dioxide to Elemental Sulfur without Generating Secondary Pollutants. 3. Kinetics of the Hydrogen Reduction of the Calcium Sulfate Powder to Calcium Sulfide

Byung-Su Kim[†] and Hong Yong Sohn*

Department of Metallurgical Engineering, University of Utah, 135 S 1460 E RM 412, Salt Lake City, Utah 84112-0114

The reduction of calcium sulfate to produce calcium sulfide is not only a part of the cyclic process for converting sulfur dioxide to elemental sulfur described in part 1 of this series but also of interest as a means of producing elemental sulfur from gypsum. This reaction was investigated using a thermogravimetric analysis technique in the absence and presence of an impregnated nickel catalyst at reaction temperatures between 973 and 1153 K and hydrogen partial pressures between 1.7 and 86.1 kPa. As an example of the reactivity of the nickel-catalyzed calcium sulfate powder, more than 95% of fresh nickel-catalyzed calcium sulfate powders was converted to calcium sulfide in 20 min at 1123 K under a hydrogen partial pressure of 86.1 kPa. Furthermore, the reactivity remained relatively intact after 10 cycles of reactions and regenerations, which is important because the solids must be reusable for repeated cycles to avoid generating secondary pollutants. The Erofeev nucleation and growth kinetics equation was found to be useful in describing the rates of the reaction, which had an activation energy of 36.2 kcal/mol (151 kJ/mol) for the fresh calcium sulfate powder and 41.0 kcal/mol (171 kJ/mol) for the fresh nickel-catalyzed calcium sulfate powder. The reaction is of first order with respect to hydrogen partial pressure for the fresh calcium sulfate powder and of order 0.26 for the fresh nickel-catalyzed calcium sulfate powder.

1. Introduction

A novel process for converting sulfur dioxide to elemental sulfur by a cyclic reaction scheme involving calcium sulfide and calcium sulfate has been developed, as described in part 1 of this series.¹ This process converts sulfur dioxide gas to elemental sulfur using calcium sulfide as a reducing agent, and the product calcium sulfate is reduced by hydrogen (or other suitable reducing agents) back to calcium sulfide. The overall process begins with calcium sulfate as the starting material and consists of the following two cyclic reactions in which the solids are repeatedly regenerated and used without net generation or consumption:



The advantage of this process is that the gaseous product from reaction (2) is essentially pure sulfur and that from reaction (1) is water vapor. The solids are reused without generating much secondary solid wastes. The process feasibility for this scheme was established in part 1 of the series,¹ and a detailed kinetics analysis for reaction (2) was presented in part 2 of the series.² In this paper, the intrinsic kinetics of the hydrogen reduction of calcium sulfate in the presence and absence

of a nickel catalyst under the conditions of negligible mass-transfer effects are analyzed.

2. Experimental Work

Experiments were carried out in a thermogravimetric analysis (TGA) unit described in detail elsewhere.^{1,3} Materials and the experimental procedure used were described in detail in ref 2. The calcium sulfate powder (99.5%) obtained from Aldrich Chemical Co. was of <44 μm size, and the procedure for impregnating this calcium sulfate powder with a nickel catalyst was described in part 1 of this series.¹

3. Experimental Results

Most experiments were continued for over 90 min, until the sample showed no further mass change. The kinetic measurements were carried out in the temperature range of 973–1153 K under the hydrogen pressure of 1.7–86.1 kPa. Fractional conversion at a particular time was determined by dividing the weight change of the solid up to that time by the total weight change at complete reaction calculated from stoichiometry.

3.1. Elimination of Mass-Transfer Effects. To check the effect of interstitial diffusion on the reaction rate of the fresh calcium sulfate powder with hydrogen, different heights between 1.0 and 3.5 mm were tested at the temperature of 1153 K under the gas flow rate of 1.7 NL/min. The reaction rate was independent of a bed height below 2.0 mm. Thus, in all of the subsequent runs, a bed height of 2.0 mm obtained by spreading 200 mg of the calcium sulfide powder as a thin layer on a shallow sample tray was used.

* To whom correspondence should be addressed. E-mail: hysohn@mines.utah.edu. Tel: 801-581-5491. Fax: 801-581-4937.

[†] Present address: Korea Institute of Geoscience & Mineral Resources, Daejeon, Korea 305–350.

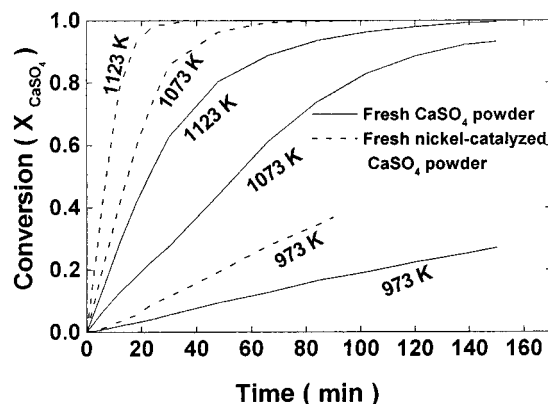


Figure 1. Comparison of the conversion of fresh calcium sulfate and fresh nickel-catalyzed calcium sulfate powders under a hydrogen partial pressure of 86.1 kPa.

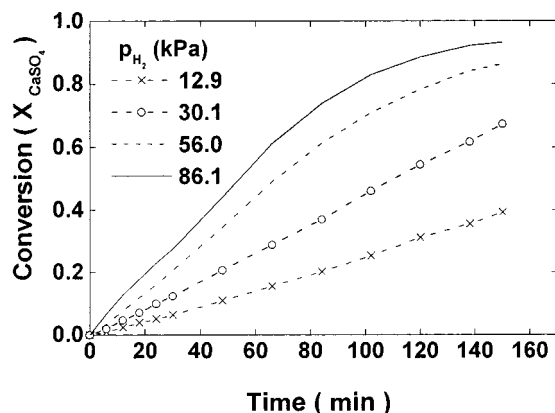


Figure 2. Effect of hydrogen partial pressure on the reaction of fresh uncatalyzed calcium sulfate at 1073 K. (All curves represent continuous TGA outputs; symbols are used just to distinguish different run conditions.)

The effect of gas flow rate on the reaction was determined in the range of 0.72–1.70 NL/min at a constant reaction temperature of 1073 K and a hydrogen partial pressure of 56.0 kPa in nitrogen. A hydrogen flow rate of 1.39 NL/min was sufficient to reduce the mass-transfer effect to a negligible level. Thus, in all of the subsequent runs, a working gas flow rate of 1.70 NL/min was used to avoid any hydrogen starvation and mass-transfer effects in the apparatus.

3.2. Effect of the Reaction Temperature. The effect of temperature on the reaction was examined by varying the temperature between 973 and 1153 K, while all other experimental parameters such as sample mass and gas flow rate were kept constant. Figure 1 shows the results for fresh noncatalyzed and nickel-catalyzed calcium sulfate powders under a hydrogen partial pressure of 86.1 kPa. It is seen that 60% of the fresh calcium sulfate powder and 95% of the fresh nickel-catalyzed calcium sulfate powder were converted to calcium sulfide in 1 h at 1073 K under a hydrogen partial pressure of 86.1 kPa.

3.3. Effect of the Hydrogen Partial Pressure. The hydrogen partial pressure was varied between 1.7 and 86.1 kPa in a nitrogen atmosphere, while the reaction temperature was kept constant at 1073 K. Typical conversion–time curves for noncatalyzed and catalyzed calcium sulfate powders are given in Figures 2 and 3, respectively. It is noted that all of the curves represent continuous TGA outputs, and the symbols are used for some curves just to distinguish different run conditions.

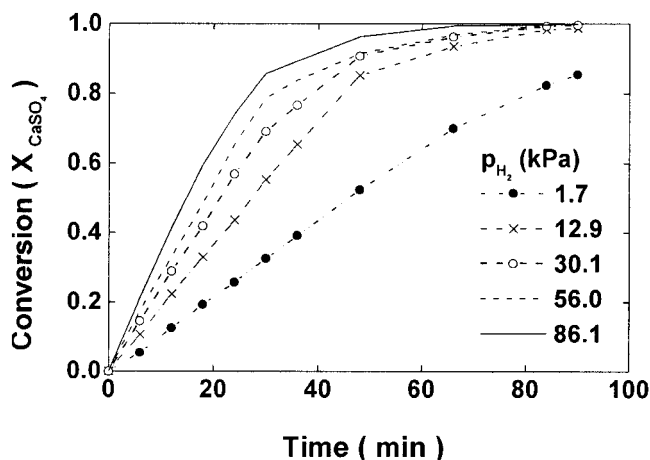


Figure 3. Effect of hydrogen partial pressure on the reaction of fresh nickel-catalyzed calcium sulfate at 1073 K. (All curves represent continuous TGA outputs; symbols are used just to distinguish different run conditions.)

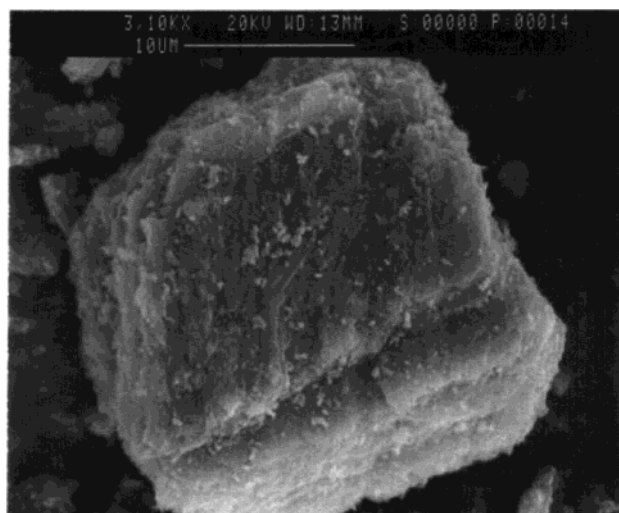


Figure 4. SEM of a fresh unreacted calcium sulfate particle.

These curves were reproducible within $\pm 3.0\%$ at each hydrogen partial pressure and show that conversion increases with increasing hydrogen partial pressure.

4. Interpretation of the Results

The particles of calcium sulfate were examined using scanning electron microscopy (SEM) before and after the reaction. Figure 4 showing fresh calcium sulfate particles before reacting indicates that the surface of the fresh calcium sulfate particles is impervious. After being reduced at 1073 K, the product calcium sulfide particles are quite porous, as was shown in part 1 of this series.¹ In a study of the reaction of calcium sulfate with carbon monoxide, Wheelock and Boylan⁴ reported that the reaction usually had an initial induction period followed by a constant and rapid period. This is a feature of nucleation and growth processes.^{5–7} Thus, it can be expected that the hydrogen reduction of calcium sulfate is likely to follow this mechanism.

4.1. Nucleation and Growth Kinetics. The interpretation of the rate data was carried out using a number of different rate equations such as the spherical shrinking-core expression, from which the Erofeev nucleation and growth kinetics proved to yield the best results. The applicability of this rate expression can be

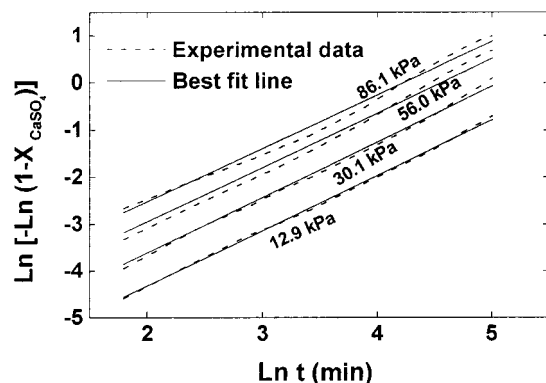


Figure 5. Plot of the results in Figure 2 according to eq 3.

expected from the fact that hydrogen adsorbs on the finely dispersed nickel islets that form the nuclei before reacting with calcium sulfate. In this rate expression, the conversion of calcium sulfate is related to the reaction time by

$$[-\ln(1 - X_{\text{CaSO}_4})]^{1/m} = k_{\text{app}2}t \quad (3)$$

where m is a constant, t is the reaction time, and $k_{\text{app}2}$ is the apparent rate constant which is given by

$$k_{\text{app}2} = b_2 k_2 f_2(p_{\text{H}_2}) = b_2 k_2 p_{\text{H}_2}^n \quad (4)$$

Here, b_2 is the stoichiometry constant ($b_2 = 1/4$ in this system, according to the formulation of Sohn⁸) for reaction (2), k_2 is the intrinsic rate constant, p_{H_2} is the hydrogen partial pressure in the bulk gas, and f_2 designates the partial pressure dependence of the rate. It is apparent from eq 3 that a plot of $\ln[-\ln(1 - X_{\text{CaSO}_4})]$ versus $\ln t$ should be linear with m as the slope and $m \ln k_{\text{app}2}$ as the intercept for $\ln t = 0$.

4.2. Analysis of the Rate Data. The rate dependency on the hydrogen partial pressure and reaction temperature was determined by first plotting the conversion–time curves of Figure 2 according to eq 3, as illustrated in Figure 5. Examination of this and other similar figures reveals that the data follow eq 3. The best-fit values of m at different SO_2 partial pressures and temperatures totaling eight runs varied between 1.13 and 1.18 for the fresh noncatalyzed calcium sulfate powder and between 1.36 and 1.39 for the fresh nickel-catalyzed calcium sulfate powder.⁹ The use of a single value of m for the same material is consistent with the mechanistic justification for the use of the nucleation and growth kinetics equation, and thus all of the calculated lines, including those in Figure 5, were plotted with an average value of m for each material, for example, 1.16 for the fresh noncatalyzed calcium sulfate powder and 1.38 for the fresh nickel-catalyzed calcium sulfate powder.

The values of $k_{\text{app}2}$ obtained from the intercepts are plotted in Figures 6 and 7 against the hydrogen partial pressure respectively for noncatalyzed and catalyzed calcium sulfate powders. As shown in Figure 6, a straight line through the origin is obtained for the noncatalyzed calcium sulfate powder, which indicates a first-order reaction with respect to the hydrogen partial pressure in a mixture with nitrogen. For the fresh nickel-catalyzed calcium sulfate powder, however, the reaction order n in eq 4 is 0.26, as shown in Figure 7. The difference in the reaction order is because nickel

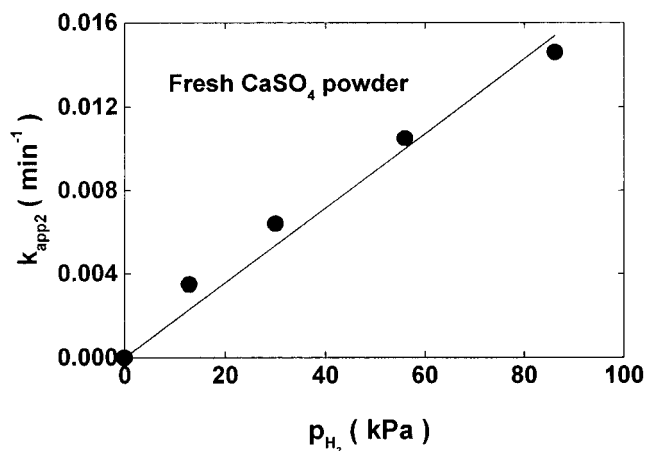


Figure 6. Dependence of the apparent reaction rate constant $k_{\text{app}2}$ on the partial pressure of hydrogen from the results shown in Figure 2.

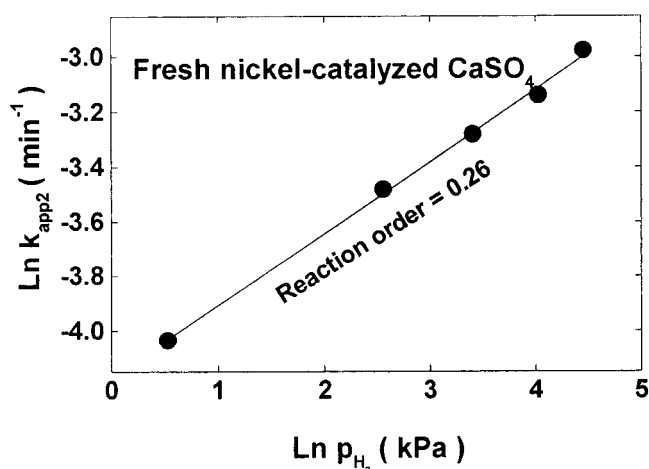


Figure 7. Dependence of the apparent reaction rate constant $k_{\text{app}2}$ on the partial pressure of hydrogen from the results shown in Figure 3.

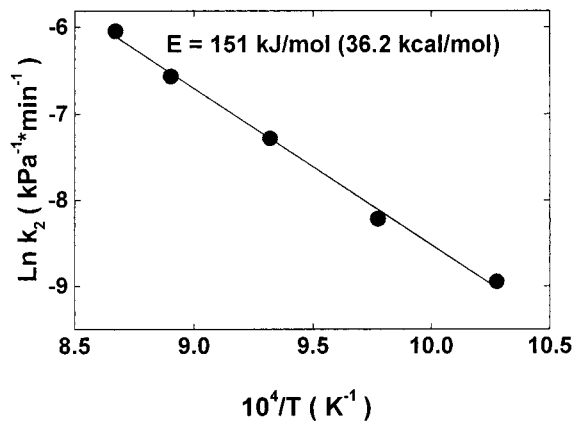


Figure 8. Arrhenius plot of k_2 for the uncatalyzed fresh calcium sulfate powder.

is a strong hydrogen adsorbent, and thus hydrogen molecules strongly adsorb and dissociate on the nickel surface, resulting in a lower overall reaction order.

The values of the rate constant, k_2 , were obtained from eq 4 at various temperatures and plotted in Figures 8 and 9. The slopes of the straight lines placed through the experimental points yield an activation energy of 36.2 kcal/mol (151 kJ/mol) for the fresh noncatalyzed calcium sulfate powder and 41.0 kcal/mol (171 kJ/mol) for the fresh nickel-catalyzed calcium

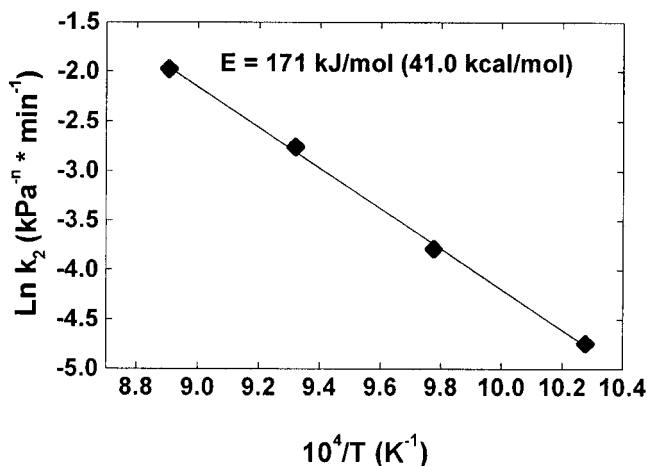


Figure 9. Arrhenius plot of k_2 for the fresh nickel-catalyzed calcium sulfate powder.

sulfate powder. These lines are represented by the following equations:

For the fresh noncatalyzed calcium sulfate powder

$$k_2 = 1.7 \times 10^4 \exp(-18200/T) \text{ kPa}^{-1} \cdot \text{min}^{-1} \quad (5)$$

For the fresh nickel-catalyzed calcium sulfate powder

$$k_2 = 1.3 \times 10^7 \exp(-20600/T) \text{ kPa}^{-1} \cdot \text{min}^{-1} \quad (6)$$

Using eqs 5 and 6, the rate of the reaction of calcium sulfate with hydrogen is represented by the following equations:

For the fresh noncatalyzed calcium sulfate powder

$$[-\ln(1 - X_{\text{CaSO}_4})]^{1/1.16} = k_{\text{app}2}t \quad (7)$$

with

$$k_{\text{app}2} = 4.3 \times 10^3 p_{\text{H}_2} \exp(-18200/T) \text{ min}^{-1} \quad (8)$$

For the fresh nickel-catalyzed calcium sulfate powder

$$[-\ln(1 - X_{\text{CaSO}_4})]^{1/1.16} = k_{\text{app}2}t \quad (9)$$

with

$$k_{\text{app}2} = 3.3 \times 10^6 p_{\text{H}_2}^{0.26} \exp(-20600/T) \text{ min}^{-1} \quad (10)$$

4.3. Reactivity of Regenerated Calcium Sulfate over Repeated Cycles. As can be seen from these rate equations as well as from Figures 1–3, the nickel catalyst greatly enhances the rate of the hydrogen reduction of calcium sulfate. Thus, the nickel-catalyzed calcium sulfate powder was used as the starting material in the determination of the reactivity of calcium sulfate over repeated reaction cycles consisting of reactions (1) and (2). The hydrogen reduction of nickel-catalyzed calcium sulfate was always allowed to proceed to completion. However, the reaction of the product calcium sulfide that follows a pore-blocking mechanism would have taken too much time to go to completion. Thus, this reaction was interrupted at certain conversion levels at different cycles, which means that regen-

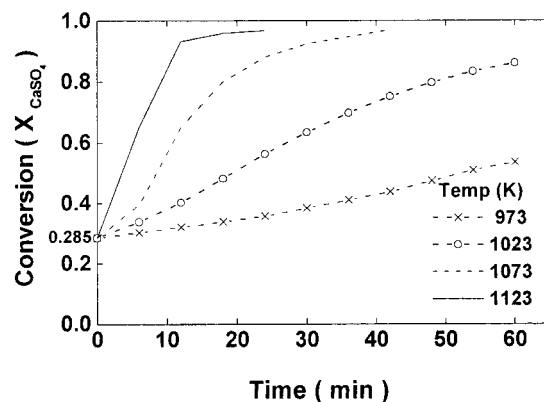


Figure 10. Effect of temperature on the reaction of nickel-catalyzed calcium sulfate powder with hydrogen in the second cycle ($p_{\text{H}_2} = 86.1 \text{ kPa}$). (All curves represent continuous TGA outputs; symbols are used just to distinguish different run conditions.)

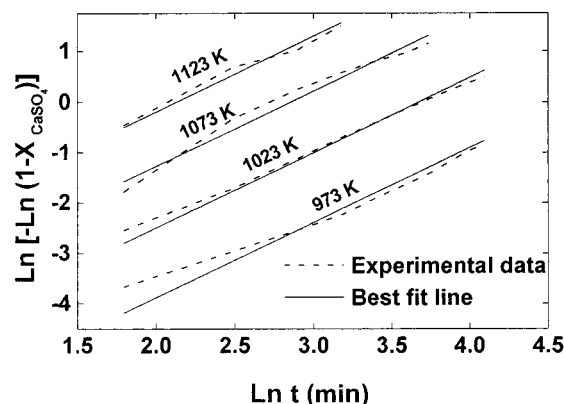


Figure 11. Plot of the results in Figure 10 according to eq 11.

erated calcium sulfate particles always contained some calcium sulfide inside them. Figure 10 shows the conversion curve for the hydrogen reduction of the nickel-catalyzed calcium sulfate powder in the second cycle (produced in the first cycle). The fraction of this unreacted calcium sulfide (and equivalent fractional conversion of calcium sulfate) was 0.285 at time zero. The conversion–time relationship for such partially regenerated particles depends on how the unreacted calcium sulfide is distributed inside each particle, which was not clearly determined in this work. The following semiempirical equation based on the above-used nucleation and growth kinetics equation, however, was found to be convenient and satisfactory:

$$\left[-\ln \left(\frac{1 - X_{\text{CaSO}_4}}{1 - X_{\text{CaSO}_4}^0} \right) \right]^{1/m} = k_{\text{app}2}t; \quad X_{\text{CaSO}_4} = X_{\text{CaSO}_4}^0 \text{ at } t = 0 \quad (11)$$

Figure 11 shows a plot of Figure 10 according to this equation with a single value of $m = 1.49$. In this case, some differences between the experimental data and the calculated lines are present, especially in the early part of the 973 K run. Although the fit for each experimental curve can be improved somewhat by using different values of m ranging between 1.47 and 1.50, it was thought to be more consistent with the mechanistic justification for the use of the nucleation and growth kinetics equation to use a single value of m for the same material, as stated earlier.

Table 1. Constants m , n , and $k_2 = k_{20} \exp(-g/T)$ for the Hydrogen Reduction of Nickel-Catalyzed CaSO_4 Powders in Different Cycles (T in K)

cycle no. generated from	$X_{\text{CaSO}_4}^\circ$	m	n	k_2	
				k_{20}	g
fresh CaSO_4	0	1.38	0.26	1.3×10^7	20 600
1	0.285	1.49	0.43	4.5×10^5	17 600
5	0.476	1.57	0.48	6.4×10^6	20 300
10	0.476	1.58	0.48	5.3×10^6	20 100

The results for calcium sulfate particles reduced in various reaction cycles at different temperatures and hydrogen partial pressures obtained by following the same procedure are summarized in Table 1. The conversion vs time curves for the reaction, at 1073 K and 86.1 kPa H_2 partial pressure, of the nickel-catalyzed CaSO_4 powder obtained from various cycles were compared with that for the noncatalyzed CaSO_4 powder in part 1 in this series.¹ The results shown there as well as in Table 1 indicate that the reactivity of nickel-catalyzed CaSO_4 is substantially higher than that of the noncatalyzed CaSO_4 powder, and its reactivity remains virtually the same until the tenth cycle. In fact, the kinetics parameters remain remarkably the same in the fifth through the tenth cycles. It is also noted that the hydrogen partial pressure dependence of the rate is close to half in all cycles, except for the fresh sample, which is consistent with the dissociation of a hydrogen molecule into two atoms upon adsorption on the nickel surface.

5. Concluding Remarks

The reaction between calcium sulfate and hydrogen was investigated using a TGA technique in the absence and presence of nickel catalyst at reaction temperatures between 973 and 1153 K and hydrogen partial pressures between 1.7 and 86.1 kPa. The reactivity of the nickel-catalyzed calcium sulfate powder was much higher than that of the noncatalyzed calcium sulfate powder at all temperatures and hydrogen partial pressures. As an example of the reactivity of the nickel-catalyzed calcium sulfate powder, more than 95% of fresh nickel-catalyzed calcium sulfate powders was converted to calcium sulfide in 20 min at 1123 K under a hydrogen partial pressure of 86.1 kPa. Furthermore, the reactivity remained relatively intact after 10 cycles of reactions and

regenerations. This is important because the solids must be reusable for repeated cycles to avoid generating secondary pollutants, as mentioned in the discussion.

The nucleation and growth kinetics was found to be useful in describing the kinetics of the reaction. The reaction has an activation energy of 36.2 kcal/mol (151 kJ/mol) for the fresh noncatalyzed calcium sulfate powder and 41.0 kcal/mol (171 kJ/mol) for the fresh nickel-catalyzed calcium sulfate powder and is of first order for the fresh calcium sulfate powder and of order 0.26 for the fresh nickel-catalyzed calcium sulfate powder.

Acknowledgment

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